

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in the Manufacture of Block Copolyamides

We, COURTAULDS LIMITED, a British Company, of 18, Hanover Square, London, W.1., England, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for the manufacture of block copolymers containing crystalline segments of a homopolyamide having repeated units of the general formula, —NH—(CH₂)_n—CO—, and synthesized by polymerising a lactam,



n being an integer and at least 5. The other segments of the block copolymer are composed of one or more different polyamides and may include a random copolyamide.

Block copolymers of this kind have been made by condensing two preformed, different, polyamide oligomers having complementary end groups which interact to form amide linkages joining the oligomers which are then segments in a high molecular weight copolymer. A critical feature of this process is that the degree of polymerisation of the segments are not necessarily the same as those of the parent oligomers, because the condensation reaction is inevitably accompanied by some transamidation.

We have devised a process in which the polymerisation of the homopolyamide occurs simultaneously with the generation of the block copolymers.

According to the present invention a polyamide oligomer having amino end groups is reacted with a polyfunctional activator as herein defined, in relative proportions such that for each amino group of the oligomer there are present at least 1.2 functional groups of the activator, and a lactam of the general formula



in which n is an integer and at least 5, containing a catalyst for the anionic polymerisation of the lactam, whereby the lactam is polymerised to form a linear homopolyamide oligomer different from the polyamide oligomer and joined thereto through the residue of the polyfunctional activator.

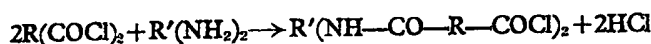
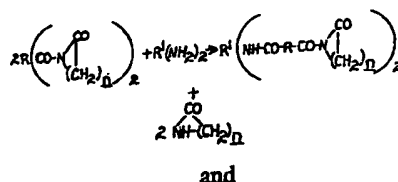
A "polyfunctional activator" for the purpose of this specification is a compound containing two or more functional groups which are (i) known to activate the anionic polymerisation of a lactam to a linear polymer at a temperature below the temperature at which the catalysts alone are effective, and (ii) capable of adding to or condensing with a primary or secondary amino group. Examples of such groups are imide, isocyanate and acyl halide and examples of general and specific polyfunctional activators are: polyacid chlorides such as phosgene, adipyl chloride, sebacyl chloride, and terephthaloyl chloride; NN' acyl bislactams such as NN' terephthaloyl - bis - caprolactam and NN' sebacyl - bis - caprolactam; and diisocyanates for example 2:4 tolylene diisocyanate and diphenyl methane diisocyanate.

In a preferred way of carrying out the process, one equivalent of the polyamide is

reacted with two equivalents of the polyfunctional activator before being brought into contact with the lactam and catalyst. The activator is covalently bound to the nitrogen atom of the terminal amino groups of the polyamide by this reaction and suffers the loss of one functional group in the process,



Similar equations can be formulated for the reaction of the polyamide with NN' acyl bislactams and with diacid chlorides respectively as follows:—



In all these reactions the polyamide has been endowed with terminal groups capable of activating the polymerisation of the lactam and acting as centres for the growth of the lactam polymer so that the block copolymer forms as the lactam is polymerised.

It is preferred that the polyamide be linear and have only two amino end groups and that the polyfunctional activator, too, should have only two functional groups; in these circumstances the polymerisation of the lactam brings about the formation of an essentially linear block copolymer.

The polyamide should not be identical with the homopolyamide of the lactam and is preferably a copolymer of two amino acids. For example it may be a copolymer of aminocaproic acid and hexamethylene adipamide salt, or a copolymer of hexamethylene sebacamide salt and another amino acid. The polyamide may also be a homopolymer for example nylon 66, nylon 610 and nylon 11.

The polymerisation catalyst for the anionic polymerisation of the lactam may be any of the known catalysts, for example, alkali metals such as sodium and lithium, alkaline earth metals such as calcium and strontium, or Grignard reagents such as methyl magnesium iodide.

The lactam is preferably ϵ -caprolactam, but other lactams for example those derived from ω -aminocaproic acid, ω -aminocaprylic acid, ω -aminocapric acid, ω -aminolauric acid and ω -aminomyristic acid are also useful.

The formation of the block copolymer takes place under conditions which are known for the anionic polymerisation of the lactam in the presence of a catalyst and activator and these conditions are milder than those

the remaining functional group being reserved to activate the polymerisation of the lactam in a subsequent stage. Thus, for example, an activator $R(NCO)_2$, having two isocyanate groups may be condensed with a polyamide polymer $R'(NH_2)_2$ having two terminal amino groups according to the equation:—

which would cause a randomisation of the polymer units through a transamidation reaction. For example, the temperature necessary for an activated lactam polymerisation is commonly as low as 160°C , and it is rarely necessary to exceed 200°C .

Block copolymers containing random copolyamide segments are particularly valuable as the low crystallinity of these segments endows the block copolymers with elastic properties. This may be made use of in fibres made by melt-extruding the copolymer, or in fibres each of which is made up of collateral components, one component being a block copolymer made according to the present invention and the other a less elastic polymer. The composite fibre is either immediately elastic and crimped, or may be made so by realising the elasticity in the block copolymer in an annealing process.

The random oligomeric copolyamide is also more soluble in the lactam than the oligomeric homopolyamide so that larger proportions may conveniently be incorporated, first in the lactam and then in the final copolymer.

The amino end groups necessary to the polyamide may readily be incorporated by making the polymer in the presence of an excess of a diamine, for example hexamethylene diamine. The excess diamine may also be used to limit the average molecular weight of the polyamide which in general should be in the range 1,000 to 6,000 and preferably in the range 2,000 to 3,500.

The invention is illustrated by the following Example in which parts by weight.

EXAMPLE

One part of an amino-ended nylon 6/66 copolymer made from 3 parts of epsilon

caprolactam to 2 parts of hexamethylene adipamide salt and having a molecular weight of 2790, was dissolved in 3.73 parts of epsilon caprolactam. The solution was dried at 120°C and at 5 mm Hg pressure under a stream of dry nitrogen for 90 minutes. Terephthaloyl bis-caprolactam (0.255 part) was added to the solution and the mixture heated at 120°C for 2 hours. A solution of sodium (0.0164 part) and caprolactam (1.29 parts) was introduced to the mixture and the temperature raised to 160°C. After 45 minutes the mixture had been transformed to a hard, light brown block of polymer. Shavings of the polymer block were soaked in glacial acetic acid for 16 hours and extracted over a period of 2 hours with hot methanol to remove soluble material. The loss of weight during the extraction was 5.4 per cent and the residual, purified block copolyamide melted at 216°C.

WHAT WE CLAIM IS:—

1. A process for the manufacture of block copolymers containing crystalline segments of a homopolyamide comprising reacting a polyamide oligomer having amino end groups and an average molecular weight of from 1,000 to 6,000 with a polyfunctional activator as hereinbefore defined in relative proportions such that for every amino group of the oligomer there are present at least 1.2 functional groups of the activator, and a lactam of the general formula



in which n is an integer and at least 5, con-

taining a catalyst for the anionic polymerisation of the lactam, whereby the lactam is polymerised to form a linear homopolyamide oligomer different from the polyamide oligomer and joined thereto through the residue of the polyfunctional activator.

2. A process as claimed in Claim 1 in which the polyamide is reacted with the polyfunctional activator before being brought into contact with lactam and catalyst.

3. A process as claimed in Claim 1 or 2 in which one equivalent of the polyamide is reacted with two equivalents of the polyfunctional activator.

4. A process as claimed in any preceding claim in which the polyfunctional activator is an NN' acyl bislactam or a diisocyanate.

5. A process as claimed in any preceding claim in which the polyamide oligomer is a random copolyamide.

6. A process as claimed in any preceding claim in which the lactam is caprolactam.

7. A process as claimed in Claim 1 carried out substantially as described in the Example.

8. A block copolymer containing crystalline segments of a homopolyamide made by the process of any preceding Claim.

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